



Short communication

Effect of conductive carbon on capacity of iron phthalocyanine cathodes in primary lithium batteries

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H I G H L I G H T S

- Nano graphene platelets (NGPs) are shown to improve iron phthalocyanine (FePc) discharge capacity.
- Capacities of up to 2050 mAh g⁻¹ FePc corresponding to the insertion of 43 Li⁺ are demonstrated.
- NGP loadings of 10 mass % demonstrate a capacity of 860 mAh g⁻¹ FePc at a rate of 1 mA cm⁻².
- FePc is shown to be a potential cathode material for next generation primary Li batteries.

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The effect of conductive carbon type and loading was examined for the iron phthalocyanine (FePc) cathode in primary lithium (Li) batteries. The use of nano graphene platelets (NGPs) as a conductive carbon was shown to increase the discharge capacity by a factor of at least 2.5 compared to typical carbon blacks and vapor grown carbon fibers. Discharge capacities of up to 2050 mAh g⁻¹ FePc, corresponding to the insertion of 43 Li⁺, were obtained for FePc based cathodes with 25% NGPs. This is the highest cathode capacity reported in literature to our knowledge. Cathodes with 10% NGP still demonstrated reasonable capacities. Electrolyte solutions based on propylene carbonate demonstrated higher discharge voltages than those with the 1.2 M lithium tetrafluoroborate in γ -butyrolactone and 1,2-dimethoxyethane (1:1 by volume).

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1. Introduction

Primary batteries are used to power many electronic devices for commercial, medical, industrial, and military applications. Future applications will most likely require batteries with higher energy and power densities. However, the energy density of primary batteries in recent years has remained relatively stagnant because of the maturation of the various systems. Lithium (Li) is an ideal anode for primary batteries because it is the most electronegative and has the highest specific capacity at 3860 mAh g⁻¹ of all metals. The energy density of primary Li batteries is limited by the capacity of the cathode active material. Table 1 shows the

energy density for common cathodes in primary Li batteries systems available today [1,2].

Metal phthalocyanines were studied as a positive electrode material for primary and secondary Li batteries by Yamaki in the 1980s [3–6]. Iron phthalocyanine (FePc) demonstrated the highest energy density of the phthalocyanines tested, 2300 Wh kg⁻¹ FePc at a rate of 0.3 mA cm⁻² [3]. The discharge capacity, 1440 mAh g⁻¹ FePc, for the above cell corresponds to a transfer of 30.5 electron equivalents per mole of FePc. Yamaki also confirmed that lithium ion (Li⁺) does intercalate between the planes of the phthalocyanine anion [5]. Typical insertion cathode materials based on transition metal oxides, like manganese dioxide, are limited to one electron transfer per transition metal [7]. Cathodes based on conversion reactions, such as carbon monofluoride (CF_x), can demonstrate even higher capacities. This reported capacity of FePc is still nearly double the theoretical capacity of the CF_x (860 mAh g⁻¹). However, these cathodes contained 50 mass % acetylene black used as

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Table 1
Comparison of common primary lithium battery chemistries.

Cathode	Theoretical capacity/mAh g ⁻¹	Discharge voltage/V	Practical energy density/Wh kg ⁻¹ battery
MnO ₂	310	3–2.5	~250
CF _x	860	2.7–2.5	350–800
SO ₂	419	2.9–2.7	260
SOCl ₂	450	3.6–3.2	275–590

a conductive carbon because of the poor electronic conductivity of FePc [3].

This research group has recently started developing FePc as an active cathode material for high capacity primary Li batteries. The use of nano featured conductive carbons commercialized in the last twenty years [8,9], particularly nano graphene platelets (NGPs), should increase the cathode's electronic conductivity while significantly reducing carbon loadings. This publication examines both the carbon type and loading on FePc discharge capacity.

2. Experimental

Iron phthalocyanine (Strem), Vulcan XC-72 carbon (Cabot), vapor grown carbon fibers (Showa Denko) were all used as-received from the suppliers. Nano graphene platelets (Angstrom Materials, Inc.) were dried for 8 h at 80 °C under vacuum, according to the supplier's instructions. Lithium perchlorate (battery grade, Aldrich), lithium tetrafluoroborate (Stella), propylene carbonate (Aldrich), γ -butyrolactone (Aldrich), and 1,2-dimethoxyethane (Novolyte) were used as received. Cathode pads were fabricated via the “mineral spirits” method [10]. The desired proportions of FePc and carbon were mixed with an aqueous Teflon dispersion (Dupont TE-3859) in methanol (99.9%, Aldrich) until a paste formed, and dried overnight. The dried material was then ground and mixed with mineral spirits to produce a dough that was kneaded to ensure good mixing of the three cathode components. The dough was calendered to form a pad with a uniform thickness. The calendered pad was then hot pressed onto a titanium grid (Dexmet) current collector, removing much of the mineral spirits. The pad was then transferred to a hot plate and finally a vacuum oven at 80 °C where it dried over night to remove residual mineral spirits and moisture. Electrodes with a geometric area of 5 cm² were then punched from this larger pad. The FePc loading, as well as pad mass and thickness, varied with pad composition and are

discussed below in section 3. All percentages used in this publication are based on mass.

The 5 cm² cathode was then layered with separator (Tonen E16) and Li metal foil (Chemetall) anode and sealed in a flexible laminate pouch. All cell contained a large excess of Li. The electrolytes used were a typical primary Li battery electrolyte consisting of 1.2 M lithium tetrafluoroborate (LiBF₄) in γ -butyrolactone (γ -BL) and 1,2-dimethoxyethane (DME) (1:1 by volume) and 1 M lithium perchlorate (LiClO₄) in propylene carbonate (PC) since it was used in the original research by Yamaki [3]. LiBF₄ in PC was also tested to see if the electrolyte salt had any effect. All electrolytes were prepared in an argon filled dry box. The completed cells were activated in the dry box to prevent exposure to air.

The solubilities of FePc in various solvents were determined by transmittance spectrophotometry at a wavelength of 350 nm using a Bausch and Lomb Spectronic 20 spectrophotometer and plastic disposable cuvettes. The conductivities of the electrolytes were measured with a Hach sension5 conductivity meter. All these tests were performed at 25 °C.

Cells were discharged using an Arbin BT-2000 battery tester. The cathodes were discharged galvanostatically at ambient temperature. At least three cells were tested for each condition and the average discharge capacity is reported. The error bars are the standard deviation for each set of tests. The cell with the median capacity was used for figures that show voltage profile during discharge.

3. Results with discussion

Table 2 summarizes the electrode properties as well as performance at a discharge current density of 0.25 mA cm⁻². All capacities and energy densities are given on a mass of FePc basis. The capacities and energy densities on a mass of electrode basis (mass of FePc, conductive carbon, and PTFE binder) can be calculated by multiplying the quantity by the mass percent of FePc divided by 100. A discussion of the results follows.

3.1. Conductive carbon type

Fig. 1 shows the voltage response during primary discharge at a current density of 0.25 mA cm⁻² for cells with 60 (mass) % FePc, 20% PTFE binder, and 20% of different conductive carbons. Vulcan XC-72 was used as a control carbon black in these studies. Vapor grown carbon fibers (VGCFs) are a commercial product that has been demonstrated to increase the mechanical strength and electronic conductivity of Li-ion battery electrodes [9]. Graphene has

Table 2
Electrode properties and performance for galvanostatic discharge at 0.25 mA cm⁻².

Carbon	Carbon/%	FePc/%	PTFE/%	FePc loading/mg cm ⁻²	Density ^a /g cm ⁻³	Capacity ^b /mAh g ⁻¹	Energy density ^b /Wh kg ⁻¹
Vulcan	20	70	10	15.3	1.1	488	722
Vulcan	20	60	20	11.7	0.9	613	
VGCF	20	70	10	11.4	1.0	502	746
VGCF	20	60	20	9.6	1.0	620	913
NGP	20	75	5	3.7	0.4	1735	2453
NGP	20	70	10	6.0	0.4	1559	2197
NGP	20	60	20	5.1	0.4	1758	2437
NGP	25	65	10	3.2	0.2	2055	2793
NGP	15	75	10	4.7	0.4	1478	2048
NGP	10	80	10	7.9	0.6	1179	1642
NGP ^c	15	75	10	4.7	0.4	1422	2386
NGP ^d	15	75	10	4.7	0.4		

^a This refers to the electrode density, i.e. the total mass of electrode (not including current collector) divided by the electrode volume.

^b Both of these quantities are the average of three tests and on a mass of FePc basis.

^c The electrolyte for these experiments was 1M LiClO₄ in PC.

^d The electrolyte for these experiments was 1M LiBF₄ in PC.

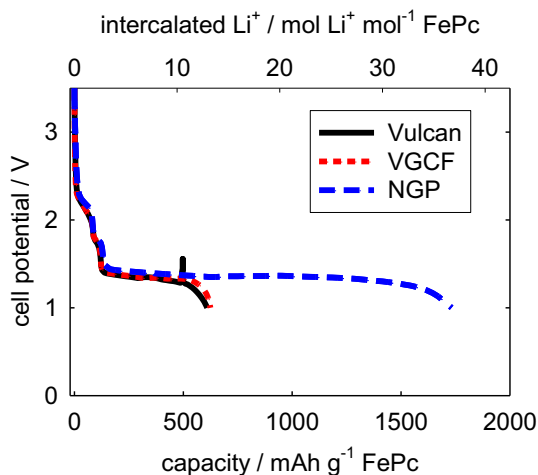


Fig. 1. Voltage profile during discharge of Li/1.2 M LiBF₄ in γ -BL:DME (1:1)/FePc cathode cell at a current density of 0.25 mA cm⁻² for different conductive carbons. The cathodes consist of 60% FePc, 20% conductive carbon, and 20% PTFE by mass. The spike on the curve for Vulcan is due to a power outage.

been demonstrated to improve lithium-ion battery performance in numerous recent publications [11–13]. The electrolyte used for these experiments was 1.2 M LiBF₄ in γ -BL:DME (1:1), a typical primary Li battery electrolyte. The voltage profile during this discharge shows three distinct features. There are two small voltage plateaus observed during the start of discharge. They may be caused by reduction of residual oxygen in the cell and intercalation of Li⁺ into the carbon. Finally, there is a voltage plateau at 1.4 V for the majority of the discharge, corresponding to insertion of Li⁺ into FePc. This is a slightly lower voltage than the 1.6 mean voltage for discharge at 0.3 mA cm⁻² reported by Yamaki and Yamaji [3]. This was most likely due to differences in the electrolyte that are discussed below.

The cells using NGPs demonstrated approximately 2.5 times higher capacity than cells with the other carbons. Fig. 1 also shows the discharge voltage is also slightly higher for the cells using NGPs. We also tested these electrodes at 1 mA cm⁻² and the cells using NGP as the conductive carbon has an average capacity of 1110 mAh g⁻¹ FePc compared to 330 for the VGCF and 250 for the Vulcan. Similar increases in capacity using NGPs were found for electrodes with 70% FePc and 10% PTFE.

As discussed in the introduction, Yamaki et al. concluded that Li⁺ does intercalate between the phthalocyanine anions by using x-ray diffraction to measure an increase in interlayer distance with increased discharge time [5]. They also observed that the concentration of Li⁺ is not uniform between different interlayer gaps [5]. This demonstrates that not all of the capacity of FePc was utilized. The BET surface areas of the carbons used here are 235 m² g⁻¹ for Vulcan, 14 m² g⁻¹ for VGCF, and 400–800 m² g⁻¹ for NGPs according to manufacturer data. The higher surface area may result in better contact between the phthalocyanine and carbon allowing for higher utilization. This is supported by a publication by Okada and Yamaki that studied the effect of particle size on discharge behavior [6]. The cathodes with a finer FePc particle had a capacity of approximately 1700 mAh g⁻¹ FePc compared to 2000 mAh g⁻¹ for the larger particle at a low current density of 0.1 mA cm⁻². However, at a high current density of 2 mA cm⁻², where electronic conduction would have a greater effect, the fine particles still have a capacity of 900 mAh g⁻¹ FePc while the capacity of the larger particle is approaching zero. High rate performance is improved because of good contact between the FePc, carbon, and electrolyte.

Fig. 2 shows the effect of FePc loading on discharge capacity for the different carbons, which may also explain the large increase in performance seen when NGPs are used as the conductive carbon. In general the capacity is higher at a lower FePc loading level. This correlation is much stronger (larger slope) in the NGP containing cells than the Vulcan and VGCF containing cells. It is noted that all the electrodes were made with similar thickness (~0.018 cm). Therefore lower FePc loading means that FePc is more diluted (volume wise) in the carbon/binder matrix, which may lead to better interfacial contact between FePc and carbon and thus improve the electronic conductivity. The reason that the NGP containing electrodes have much lower FePc loading is due to its much lower bulk density compared to Vulcan and VGCF. It was difficult to obtain reproducible quantitative measurements of either the loose or tapped bulk density for the nano-carbons, however, qualitatively the bulk densities are in the order of NGP << VGCF < Vulcan XC72. For reference, the literature value for tapped bulk density of Vulcan XC72 is 0.264 g cm⁻³ [14] and VGCF is 0.04 g cm⁻³ [15]. The tapped bulk density of NGP is approximately one order of magnitude lower than the VGCF. We are planning on studying this system by nuclear magnetic resonance, X-ray diffraction and electron microscopy techniques to obtain a better understanding of the fundamental electrochemical processes and the reason for the increase in capacity demonstrated by cells with NGPs. Regardless of the reasons, the capacity was significantly increased when NGPs are used as conductive carbon.

Finally, we tested cells with a Li anode and 80% NGP with 20% PTFE binder cathode to confirm this increase in capacity was not related to Li⁺ insertion into the NGPs or electrolyte decomposition on the NGPs (data not shown). The cells were discharged galvanostatically at a current density of 0.25 mA cm⁻² with different electrolytes. All cells demonstrated capacities less than 100 mAh g⁻¹ NGP. This corresponded to 1.7% of the average demonstrated capacity being related to graphene for the cathodes containing 60% FePc, 20% NGP, and 20% PTFE in 1.2 M LiBF₄ in γ -BL:DME (1:1). Therefore the increase in capacity was not related to processes involving only the NGP.

3.2. FePc/graphene/binder ratios

Fig. 3 shows the capacity and Fig. 4 shows the energy density for cathodes containing varying amounts of FePc, NGP, and PTFE. To calculate the mass % of FePc, subtract the mass percent of NGP and PTFE from 100. The percentage of binder has no significant effect on the capacity and energy density on a mass of FePc basis. A linear increase in capacity and energy density with NGP loading is observed for 0.25 mA cm⁻². The average capacity is 2050 mAh g⁻¹

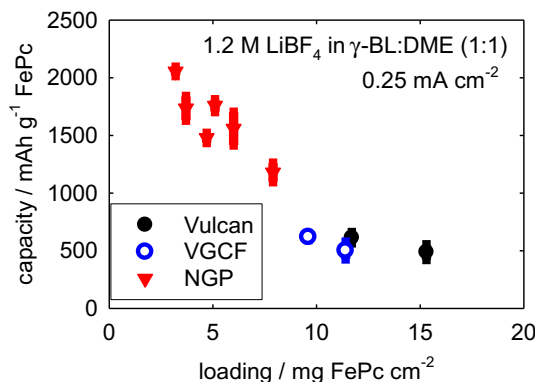


Fig. 2. Effect of FePc loading on discharge capacity for cells discharged in 1.2 M LiBF₄ in γ -BL:DME (1:1) at a current density of 0.25 mA cm⁻².

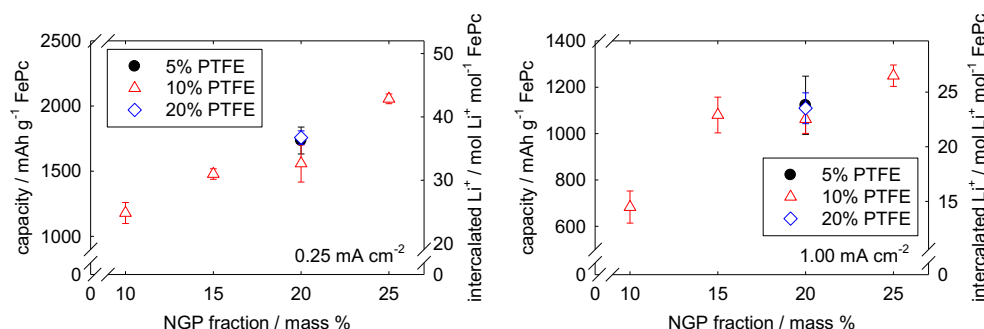


Fig. 3. Effect of the cathode mass ratio of FePc, graphene, and PTFE on the discharge capacity of primary Li cells with a 1.2 M LiBF₄ in γ -BL:DME (1:1) electrolyte at current densities of 0.25 (left) and 1.00 (right) mA cm⁻². The capacity is on a per gram of FePc basis.

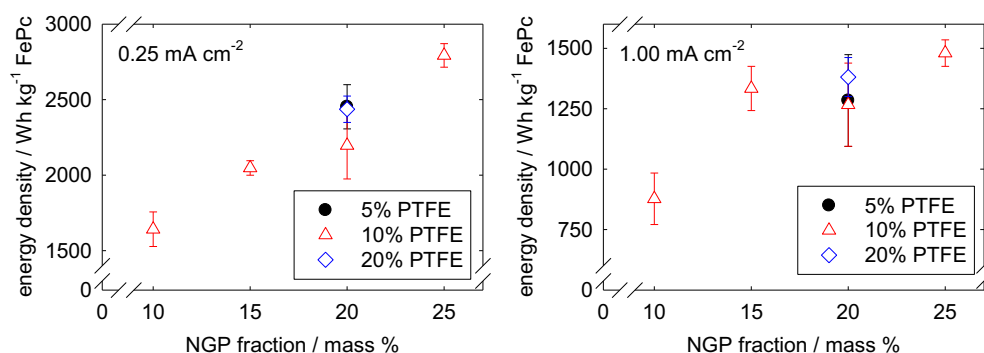


Fig. 4. Effect of the cathode mass ratio of FePc, graphene, and PTFE on the energy density of primary Li cells with a 1.2 M LiBF₄ in γ -BL:DME (1:1) electrolyte at current densities of 0.25 (left) and 1.00 (right) mA cm⁻². The energy density is on a per gram of FePc basis.

FePc for cells containing 25% NGP. This corresponds to the insertion of 43 Li⁺. The increase in capacity with NGP loading for 1 mA cm⁻² is not linear. As discussed above, the increase in capacity with increasing NGPs appears to be directly related to the improving interfacial contact between FePc and NGPs. However, at the higher current density, the rate limiting step may be Li⁺ transport through the FePc. Therefore, decreasing the FePc loading no longer affects the capacity because it is limited by the poor kinetics of the system. Cells with a low NGP loading of 10% still demonstrate capacities of over 680 mAh g⁻¹ FePc at a rate of 1 mA cm⁻².

The energy density based on total electrode mass is more important than just active material for design of a practical battery. Fig. 5 shows the energy density at 0.25 and 1.00 mA cm⁻² on an electrode basis. The energy density increased as the binder is decreased for the 20% NGP since the relative amount of active

material is increased. However, for the 1 mA cm⁻² discharge the average energy density increases from 700 Wh kg⁻¹ electrode at 10% NGP to 1000 Wh kg⁻¹ electrode for 15% NGP and then remains relatively flat. Figs. 3 and 4 are based on mass of active material so the behavior is not necessarily expected to be the same in Fig. 5 since it is based on total electrode mass, i.e. active and inactive components. The FePc loading, shown in Table 2, should also be high to maximize the absolute capacity.

Three electrode compositions demonstrated better performance than the others. They were the (mass % FePc/NGP/PTFE) 75/15/10, 75/20/5, and 65/25/10. The low amount of binder used in the 75/20/5 cathodes made them difficult to work with, both in fabricating the pad and handling the pad afterward. The FePc loading was lowest for the 65/25/10 out of all the cells tested. Therefore the 75/15/10 composition was selected to run further tests.

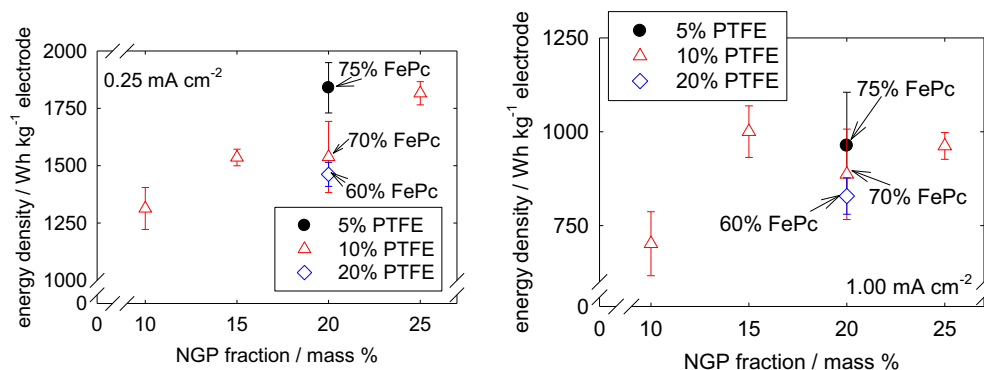


Fig. 5. Effect of the cathode mass ratio of FePc, graphene, and PTFE on the energy density of primary Li cells with a 1.2 M LiBF₄ in γ -BL:DME (1:1) electrolyte at current densities of 0.25 (left) and 1.00 (right) mA cm⁻². The energy density is on a per gram of cathode (FePc + NGP + PTFE) basis.

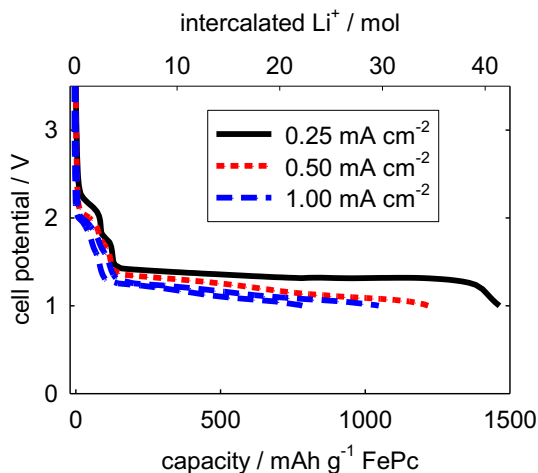


Fig. 6. Voltage profile during discharge of Li/1.2 M LiBF₄ in γ-BL:DME (1:1)/FePc cathode cell for different current densities. The FePc cathode consists of 75% FePc, 15% NGP, and 10% PTFE by mass.

Fig. 6 shows the typical discharge profile for different current densities of primary Li cells with the 75/15/10 cathode and 1.2 M LiBF₄ in γ-BL:DME (1:1) electrolyte. The cells all demonstrate high capacities over 1000 mAh g⁻¹ FePc. The 0.5 and 1.0 mA cm⁻² discharge have low average discharge voltages due to higher kinetic overpotentials.

The use of NGPs increases the cathode capacity at lower carbon loadings when comparing to previous reports. Yamaki and Yamaji reported a capacity of 1440 mAh g⁻¹ FePc for cells containing 50 mass % acetylene black at a discharge rate of 0.3 mA cm⁻² [3]. The cell energy density decreased to 730 Wh kg⁻¹ of FePc for a discharge rate of 1 mA cm⁻² [3]. Fig. 3 (left) shows that loadings of 15% and greater NGPs demonstrate a higher capacity up to 2050 mAh g⁻¹ FePc at a slightly lower rate of 0.25 mA cm⁻². Fig. 4 (right) shows that loadings of 10% NGP and greater demonstrate a higher energy density up to 1500 Wh kg⁻¹ FePc than the previous reported values with 50% acetylene black conductive carbon at a discharge current density of 1 mA cm⁻². A later publication showed improved capacities of approximately 2000 mAh g⁻¹ FePc at 0.1 mA cm⁻² and 1000 mAh g⁻¹ FePc at 1 mA cm⁻² for cathodes containing 48% Ketjen black EC conductive carbon [6]. Fig. 3 (left) shows the 25% NGP cathode demonstrates a higher capacity at a higher current density of 0.25 mA cm⁻². Fig. 3 (right) shows better performance at 1 mA cm⁻² for cells containing 15% or more NGPs.

3.3. Electrolyte type

Other electrolytes were tested in attempt to raise the discharge voltage. Table 3 is a summary of the electrolytes' conductivity and FePc solubility. Fig. 7 shows that the use of 1 M LiClO₄ in PC, the electrolyte used in the original FePc study by Yamaki and Yamaji [3], results in a higher average discharge voltage of 1.7 V. 1 M LiBF₄ in PC

Table 3
Some properties of electrolytes.

Electrolyte	Solubility/mg FePc kg ⁻¹ solvent	Conductivity/mS cm ⁻¹
1.2M LiBF ₄ in γ-BL:DME (1:1)	57	9.8
1 M LiClO ₄ in PC	30	5.5
1 M LiBF ₄ in PC	29	3.6
PC	35	
γ-BL	91	
DME	33	

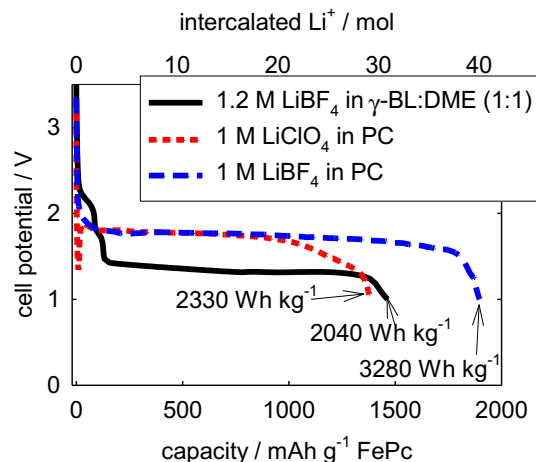


Fig. 7. Typical voltage profile during discharge of a cathode consisting of 75% FePc, 15% NGP, and 10% PTFE at a current density of 0.25 mA cm⁻² for different electrolytes.

was tested to study the effect of electrolyte salt. This electrolyte demonstrated a much better performance, an average capacity of 1914 mAh g⁻¹ FePc at a discharge voltage of 1.7 V. The cause for the increase in capacity using LiBF₄ is not currently clear. This increase is not related to conductivity since the 1.2 M LiBF₄ in γ-BL:DME (1:1) demonstrates the highest conductivity but lowest discharge voltage. The solubility of FePc is nearly double for this electrolyte compared to the electrolytes with PC as a solvent. This could cause two problems. The first is FePc in the electrolyte may react with Li, increasing Li anode resistance. The second is there will be less FePc in the cathode, so the current on a FePc particle (mA g⁻¹ FePc) will be higher. Since the current is higher the overpotential will be greater, resulting in a lower discharge voltage. It should be noted that FePc may react with PC electrolyte solvent at potentials under 1.3 V vs Li/Li⁺ [4]. However, only a small percentage of the discharge occurs at potentials lower than 1.3 V so it is not a large problem for the primary system.

These results show that PC or mixtures of PC and DME (to increase conductivity) are better suited as electrolyte for the Li/FePc system than typical electrolytes for primary applications.

4. Conclusions

The use of NGP as a conductive carbon was shown to increase the discharge capacity by a factor of over 2 compared to typical carbon blacks and VGCFs. Discharge capacities of up to 2050 mAh g⁻¹ FePc, corresponding to the insertion of 43 Li⁺, were obtained for FePc based cathodes with 25% NGPs. This is the highest capacity ever reported for a lithium battery cathode to our knowledge. Furthermore, these capacities were obtained at nearly half of the conductive carbon loading of previous reports for this system. Cathodes with 10% NGP still demonstrated reasonable capacities. Electrolytes based on propylene carbonate demonstrated higher discharge voltages than those with the 1.2 M LiBF₄ in γ-BL:DME (1:1). FePc was shown to be a viable candidate for next generation primary Li batteries, however, problems with limited rate capabilities, solubility of FePc in aprotic organic electrolytes, and low electrode density must be addressed before the system is commercialized.

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References

- [1] D. Linden, T.B. Reddy, in: T.B. Reddy (Ed.), *Linden's Handbook of Batteries*, fourth ed. McGraw-Hill Professional, New York, 2010, pp. 8.3–8.18.
- [2] T.B. Reddy, in: T.B. Reddy (Ed.), *Linden's Handbook of Batteries*, fourth ed. McGraw-Hill Professional, New York, 2010, pp. 14.1–14.9.
- [3] J. Yamaki, A. Yamaji, *J. Electrochem. Soc.* 129 (1982) 5–9.
- [4] M. Arakawa, J. Yamaki, T. Okada, *J. Electrochem. Soc.* 131 (1984) 2605–2607.
- [5] S. Okada, J. Yamaki, T. Okada, *J. Electrochem. Soc.* 136 (1989) 340–344.
- [6] S. Okada, J. Yamaki, *J. Electrochem. Soc.* 136 (1989) 2437–2440.
- [7] B. Scrosati, J. Garche, *J. Power Sources* 195 (2010) 2419–2430.
- [8] P.V. Kamat, *J. Phys. Chem. Lett.* 2 (2011) 242–251.
- [9] M. Endo, Y.A. Kim, T. Hayashi, K. Nishimura, T. Matusita, K. Miyahsita, M.S. Dresselhaus, *Carbon* 39 (2001) 1287–1297.
- [10] O. Crowther, B. Meyer, M. Morgan, M. Salomon, *J. Power Sources* 196 (2011) 1498–1502.
- [11] J.G. Radich, P.J. McGinn, P.V. Kamat, *Electrochem. Soc. Interface* 20 (2011) 63–66.
- [12] A. Abouimrane, O.C. Compton, K. Amine, S.T. Nguyen, *J. Phys. Chem. C* 114 (2010) 12800–12804.
- [13] N. Zhu, W. Liu, M.Q. Xue, Z.A. Xie, D. Zhao, M.N. Zhang, J.T. Chen, T.B. Cao, *Electrochim. Acta* 55 (2010) 5813–5818.
- [14] http://www.cabot-corp.com/wcm/download/en-us/sb/VULCAN_XC72-English.pdf (accessed 30.05.12).
- [15] <http://www.sdcc.com/documents/VGCF-H.pdf> (accessed 30.05.12).